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Oil Shale Process Model (OSP) Theory Manual

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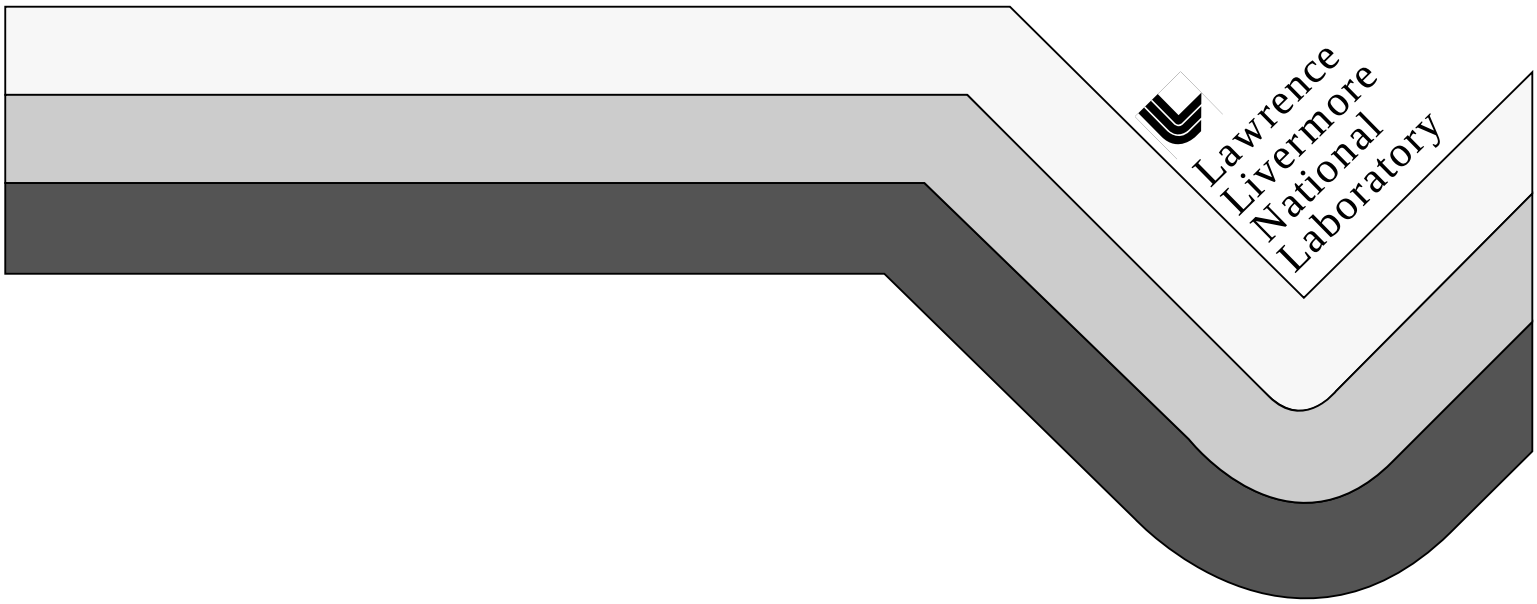

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Oil Shale Process Model

(OSP)

Theory Manual

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PREFACE

The Oil Shale Process (OSP) model has proven to be a useful tool for the analysis of the steady-state operation of Lawrence Livermore National Laboratory's Hot–Recycled–Solids 4 tonne-per-day Pilot Retort (4TU-Pilot). This manual has been developed to guide a user through the theoretical basis for equations, models, and correlations in the unit operation modules used in the OSP code.

The OSP code has been developed for generalized chemical process simulation of the HRS oil shale retort. Several of the common unit operations encountered in industrial chemical process design are included in the OSP code, including packed and fluidized bed reactors, splitting and mixing operations, and a dilute flow lift–pipe. A set of chemical species and reactions related to oil shale processing are available for incorporation into a given simulation.

Two other manuals complete the documentation for the OSP code, the "Oil Shale Process Model (OSP) Code Development Manual" and the "Oil Shale Process Model (OSP) Users Manual". These manuals should be referenced to learn coding specifics and how to use OSP for process simulation.

INTRODUCTION

The computer code OSP has been developed to allow a generalized-steady-state-numerical simulation of the Hot–Recycled–Solids (HRS) Oil Shale Process to be constructed. The HRS process is being developed at Lawrence Livermore National Laboratory (LLNL) for the aboveground retorting of Oil Shale. The OSP code helps research staff to critically analyze operation of LLNL's 4TU-Pilot. It can also be used to test the consistency of laboratory, as well as pilot scale, results.

This manual describes the theoretical basis for the user selectable modules used in the OSP code. Included in this description are specific references for correlations and computational procedures. Two other manuals have been developed to describe other aspects of the OSP code. The "Oil Shale Process Model (OSP) Code Development Manual" describes the source coding details used in the OSP code and how to make changes and additions to the code. The "Oil Shale Process Model (OSP) User's Manual" describes the requirements for the user generated input file; its organization, format, and content.

Only mass and energy balances are performed between and over unit operation modules. Therefore, only mass and energy conservation equations need to be addressed in this manual. The equation of momentum, pressure balances and other force related aspects must be determined independently from the results of this code. In addition, overall gas and solid flow rates through and between units are established by the user, using other relationships not addressed by OSP code.

The OSP code uses information contained in a user supplied input file to select the order, number, and type of computational unit operations used in a simulation. The chemical species and the number and type of chemical reactions occurring in a unit operation are also specified in the input file as are initial estimates for processing conditions, stream flow rates, and chemical compositions.

CODE STRUCTURE

The OSP code has been structured in a generalized manner so that any number of unit operations can be added to a process simulation in a convenient and efficient manner. The type of units used in a simulation can be selected from those units in the code package. The number and type of chemical reaction steps and the chemical reaction stoichiometry can be changed by modifying the user supplied input file.

The code is structured so that the main routine acts as a controller for the code. It allows lower level unit operation modules to perform initialization, computation, and final summary printing and reporting steps.

The unit operation modules, which are contained in subroutines, are called by the main, controller routine. The type of computational unit operation modules supplied in the

OSP code have been selected to allow one to simulate the HRS process pilot plant. The principle unit operations used in the HRS process are listed below:

° Packed–Bed Pyrolyzer

° Lift–Pipe for Solids Transport and Combustion

° Delayed-Fall Combustor

° Fluidized–Bed for Solids Mixing and Reaction

Each of these unit operations are simulated with one or more computational modules. The modules consist of an initialization section, a computational section, and a summary-report generation section. The chemical reactions considered in specific computational unit operation module are specified in the input file.

The unit operation modules are connected to each other and to specified system input and output streams with one or more process streams. A gas process stream is characterized with a pressure, molar flow rate, composition and temperature. A liquid process stream is characterized with a mass flow rate, composition, and temperature. A solid process stream is characterized with a mass flow rate, composition, temperature, particle size, and porosity. A discretized particle size distribution can be simulated by using several solids streams, one for each size class. Initialization of the independent process streams is performed using information contained in the input file.

UNIT OPERATION MODULES

In this section, the computational modules, presently in the OSP code, are briefly described and underlying equations are presented as appropriate. Some references to module parameters are made, but for a complete list of user selectable parameters see the "Oil Shale Process Model (OSP) User's Manual" Appendix A. Before describing each module a discussion of common features of the reactor modules is presented.

There is a group of 6 modules which are the primary computational modules of OSP and represent different types of reactors which allow changes in composition to be computed which incorporate kinetic rate expressions. These reactor modules make use of two underlying computational models, the plug-flow model and the well-mixed model. The underlying models define the basic flow geometry. In the plug-flow model it is assumed that all materials are moving co-currently in a single direction, however the velocities of various components may be different. In the well-mixed model it is assumed the system is well mixed and there is therefore no spatial resolution. The CO_CURRENT, LIFT_PIPE and PACKED_BED modules use the plug-flow model while the CNTR_CURRENT, CSTR and FLUID_BED modules make use of the well-mixed model.

The Plug-Flow Model

The plug-flow model assumes that gases, solids and liquids are moving co-currently with a specified velocity for the solid streams. Energy and material balances are written as appropriate for this geometry. Energy and material transport along the resolved dimension is allowed only by convection.

The model allows for only one liquid and one gas stream, but allows multiple solid streams to be defined.

For each solid stream the following equation for species flow is defined

$$\frac{dF_{s_i}}{dz} = AS_{s_i}.$$

Where F_{s_i} is the flow of solid species *i* in the flow direction, *z*, *A* is the cross sectional area of the system and S_i is the source / sink of species *i*. S_{s_i} is written in terms of reaction rates using

$$S_{s_i} = N_p \sum_{j=1}^{n} a_{ij} R_j .$$

Where N_p is the number of particles per unit volume, a_{ij} is the stoichiometric coefficient for reaction *j* and species *i*, and R_j is the rate of reaction *j* per particle. The number of particles per unit volume is computed for each solid stream using

$$N_p = \frac{F_s}{v_s A V_p \rho_s},$$

where F_s is the flow rate of the stream, v_s is the velocity of particles in the solid stream, V_p is the volume of a particle in the stream, and ρ_s is the density of a particle. The particle velocity is an input to the model and is treated as a constant.

Similar equations are written for the gas flow

$$\frac{dF_{g_i}}{dz} = AS_{g_i},$$

and for liquid flow

$$\frac{dF_{l_i}}{dz} = AS_{l_i}.$$

Species mass and mole fractions can be defined from these fluxes in a straightforward manner as needed. Gas density is obtained from the ideal gas law and solid density is found using

$$\rho_s^* = \sum_{i=1}^{n_s} \left(x_{s_i} \rho_i^* \right),$$

$$\varepsilon_s = 1 - \frac{\sum_{i=1}^{n_s} F_{s_i}}{F_p V_p \rho_s^*},$$

and

$$\rho_s = (1 - \varepsilon_s)\rho_s^*.$$

Where ρ_s^* is the density of the solid matrix, n_s is the number of solid species, x_{s_i} is the mass fraction of solid species *i*, ρ_i^* is the density of pure species *i*, ε_s is the internal particle porosity, F_p is the flow rate of particles, V_p is the volume of a particle, and ρ_s is the effective density of the whole particle. These relations are applied independently to each solid stream.

Superficial gas velocities are defined as needed using the gas density and the total gas flux. Superficial liquid velocities are assumed equal to the gas velocity.

An energy balance equation for each solid stream is written in terms of its average temperature.

$$\frac{dT_s}{dz} = \frac{AN_p}{F_s c_s}\left(H_R - A_p h(T_s - T_g) - q_{rad}\right).$$

Here T_s is the average solid temperature, c_s is the effective solid heat capacity, H_R is a heat of reaction term defined below, A_p is the effective area of a particle, h is the gas solid heat transfer coefficient, T_g is the gas temperature, and q_{rad} is a radiant heat transfer term also defined below.

Because the reactions considered to date are all heterogeneous the heat effects from reaction have been associated with the solid stream. The heat of reaction term is thus defined using the following relation

$$H_R = \sum_{i=1}^{n_g}\left(S_{g_i} H_{g_i}\right) + \sum_{i=1}^{n_s}\left(S_{s_i} H_{s_i}\right) + \sum_{i=1}^{n_l}\left(S_{l_i} H_{l_i}\right).$$

Where the *H*'s are enthalpies evaluated at their respective phase temperatures.

The radiation term, q_{rad}, is meant to make some allowance for radiative heat transport from the solid material. The basic assumption is that the particles radiate to a wall and the wall then transfers heat to the gas phase. The model adjusts the wall temperature until a balance between solid to wall and wall to gas is obtained. The net effect is to enhance the heat transfer between solid and gas. The radiative term for a given solid stream is given by

$$q_{rad} = A_p v_f \varepsilon_r \sigma\left(T_s^4 - T_w^4\right).$$

Here v_f is a view factor, ε_r is an emissivity, σ is the Stefan-Boltzmann constant, and T_w is the local wall temperature. The local wall temperature is computed as part of the

calculation by finding the value at which the radiant heat flux to / from the wall is just balanced by the convective flux to / from the wall.

Finally, a single energy balance is written for the combined liquid and gas phases. This is done since the liquid and gas temperatures are assumed equal by the model.

$$\frac{dT_g}{dz} = \frac{1}{\left(F_g c_g + F_l c_l\right)} \left\{ A \sum_{n=1}^{n_p} \left\{ A_{p_n} N_{p_n} \left[h_n \left(T_{s_n} - T_g \right) + q_{rad_n} \right] \right\} - q_h \right\}.$$

In this equation a subscript *n* is used to designate quantities associated with particles of solid stream *n*. There are n_p solid streams. A wall to gas heat flux in addition to that implicit in the radiative transport model is defined through the q_h term. This term is defined by

$$q_h = h_{wall} (T_g - T_{wall}) \pi D$$

where h_{wall} is the wall to gas heat transfer coefficient, T_{wall} is the wall temperature and D is the diameter of the system. This heat transfer term is defined independent of the radiative transport model.

The ideal gas law is used to compute gas molar densities and this in turn is used with gas flow rate and reactor cross sectional area to compute gas velocities at each location in the system. Relative solid gas velocities used in transport correlations are obtained by taking the difference between the gas velocity and each solid stream's particle velocity.

The solution of the system of o.d.e's is obtained using LSODE (Hindmarsh, 1981) and initial conditions supplied from input stream values. Each reactor module which uses this model sets input parameters appropriate for reactor geometry simulated.

The Well-Mixed Model

The well-mixed model assumes that gases, solids and liquids are well mixed. Energy and material balances are written as a system of nonlinear equations which defines the overall changes between input and output values. The model allows for only one liquid and one gas stream, but allows multiple solid streams to be defined.

A species balance is written for each solid stream and each species *i*

$$F_i^O = F_i^I - V S_{s_i}^R + V S_{S_i}^P,$$

Here the superscript *I* refers to the inlet and the *O* to the outlet of the reactor. V is the reactor volume. The source terms, $S_{s_i}^R$ and $S_{s_i}^P$ are defined similar to the source terms in the above discussion of the plug-flow model, except that the superscripts *R* and *P* refer to reactants and products respectively, and the signs are all taken as positive. This division of source terms allows the writing of the energy balance equations, below, to be accomplished more easily. The particle number density, N_p , used in the source term relations is not computed by the model, as is the case in the plug-flow model, but,

rather, it is an input parameter to the model and must have been set for each solid stream.

A species balance is also written for the gas and liquid phases.

$$F_{g_i}^O = F_{g_i}^I - VS_{g_i}^R + VS_{g_i}^P,$$

and

$$F_{l_i}^O = F_{l_i}^I - VS_{l_i}^R + VS_{l_i}^P.$$

The energy balances are more complicated than the material balances because of the need to carefully handle the temperatures associated with the gas and liquid phases, and the individual solid streams.

For each solid stream the following energy balance is written

$$\sum_{i=1}^{n_i}\left[F_{s_i}^I H_{s_i}^{T_s^I}\right] + \sum_{n=1}^{n_g}\left[F_{g_i}^I H_{g_i}^{T_g^I}\right] + \sum_{n=1}^{n_l}\left[F_{s_i}^I H_{l_i}^{T_l^I}\right]$$
$$= VN_p A_p\left[h\left(T_s - T_g\right) + q_{rad}\right] + \sum_{i=1}^{n_i}\left[F_{s_i}^O H_{s_i}^{T_s^O}\right] + \sum_{n=1}^{n_g}\left[F_{g_i}^O H_{g_i}^{T_g^O}\right] + \sum_{n=1}^{n_l}\left[F_{l_i}^O H_{l_i}^{T_l^O}\right]$$

The superscripts on the species enthalpies, *H*, are the temperature at which the enthalpies are to be evaluated. The temperatures in the solid / gas heat transfer term do not have a superscript to relate them to inlet or outlet. This is because the model has the ability to use weighted values for process parameters in the reactor. These weighted values are used to compute transport properties and reaction rates. The most robust assumption is that these average properties are equal to the exiting properties. This is the classical assumption for a cstr (continuously stirred tank reactor) and in general allows a satisfactory solution for output streams to be found regardless of inlet stream composition.

As in the plug-flow model, the radiation term, q_{rad}, is meant to make some allowance for radiative heat transport from the solid material. The basic assumption is that the particles radiate to a wall and the wall then transfers heat to the gas phase. The model adjusts the wall temperature until a balance between solid to wall and wall to gas is obtained. The net effect is to enhance the heat transfer between solid and gas. The radiative term for a solid stream is given by the same equation as used above in the plug-flow model.

The energy balance for the combined gas and liquid phases is

$$\sum_{n=1}^{n_p}\left[N_{p_n} VA_{p_n} h_n (T_{s_n} - T_g)\right] + \sum_{i=1}^{n_g}\left[\left(F_{s_i}^I - VS_{g_i}^R\right) H_{g_i}^{T_g^I}\right] + \sum_{i=1}^{n_g}\left[VS_{g_i}^P H_{g_i}^{T_g^O}\right]$$
$$+ \sum_{i=1}^{n_l}\left[\left(F_{l_i}^I - VS_{l_i}^R\right) H_{l_i}^{T_l^I}\right] + \sum_{i=1}^{n_l}\left[VS_{l_i}^P H_{l_i}^{T_l^O}\right]$$
$$= \sum_{i=1}^{n_g}\left[F_{g_i}^O H_{g_i}^{T_g^O}\right] + \sum_{i=1}^{n_l}\left[F_{l_i}^O H_{l_i}^{T_l^O}\right]$$

The subscript on the variables in the first term refer to the n^{th} solid stream.

Gas-solid relative velocities needed for the transport correlations are input parameters to the model and must be defined for each solid stream.

The above equations have as unknown quantities the solid species flow exiting the reactor for each solid stream, the temperature of each exiting stream, the gas and liquid species flows exiting the reactor and their temperatures. The model assumes that the gas and liquid temperatures are equal. The primary interest is in gas/solid systems and as a result the implementation of the liquid phase is rudimentary.

The system of nonlinear equations is solved using the LSODE o.de. package. This is accomplished by forming a residual from each of the above balance equations. This residual is then weighted and set equal to a derivative of one of the unknowns most closely associated with the particular balance equation (e.g. for the gas/liquid energy balance the gas outlet temperature is used). After establishing initial guesses the system of equations is solved to steady-state by LSODE. At steady-state the derivatives are zero and thus the residuals are all zero which means a suitable solution has been found. This method of solution has two advantages. First, the LSODE package is already incorporated into OSP and secondly, the treatment helps guide the solution toward a desirable solution set. Since the equations are nonlinear there is potentially more than one answer set. For the most part all but the desired solutions tend to be non physical (e.g. negative temperatures or composition). Consequently, having the solution evolve in a quasi-time-dependent manner from an initial estimate is desirable.

A scale factor of one is used to multiply the residuals to form the time derivatives for all variables except solid temperatures. For solid temperatures the following scale factor is used

$$\text{scale factor} = \frac{0.001}{\left|F_s^I\right| + \left|F_s^O\right|}.$$

If this factor is less than one, a value of one is used.

Each reactor module which uses this model sets input parameters appropriate for reactor geometry simulated.

ATTRITION Module

The ATTRITION module is used to simulate the changes in particle sizes that occur in the processing of oil shale. Because the mechanism responsible for the attrition can differ at different locations in the process a number of different types of attrition have been implemented. TYPE=1 attrition assumes that the composition of a solid particle that is to undergo attrition is uniform spatially. The mass fraction of solid that attrits in this module is an input parameter. The chemical composition of the original, parent solid particle, and the daughter materials generated in the attrition process are the same. A solid stream with a single particle size can be broken up into as many as 10 daughter streams each with its own diameter. The user supplies values which sets the fraction of the parent stream which is transformed into each daughter stream and the size of the particles in each new stream. TYPE=4 attrition is essentially the same, except only two output streams are allowed. The diameter of the first stream is derived from that of the input stream by assuming loss of the required fraction of mass. The second stream has a diameter set by user input. TYPE=5 attrition is also essentially the same as TYPE=1, except that the size of the newly created particles are not given explicitly, but are instead specified as a fraction of the original particle size.

In TYPE=2 and 3 attrition, it is assumed that the parent stream gives rise to only two daughter streams. The composition of the parent particle and the daughter streams are in general different. This type of attrition is typically used to simulate the attrition of a particle that has an ash layer at its surface. The ash layer differs from the material in the interior of the particle because it has been depleted of carbon (char). The original, or core, density of the char is obtained from the stream variable PROP_SOLID(1,n), where n is the internal stream number of the parent particle stream. In TYPE=2 attrition, it is assumed that a specified mass fraction of this exterior layer of ash is attrited. In TYPE=3 attrition, it is assumed that the layer thickness of the ash is maintained equal to or less than a specified value. If a particle enters the module with an ash layer greater than the specified thickness the particle attrits to a new particle size which has an ash layer equal to the specified value. In both cases the diameter of the attrited ash particles is a user defined parameter.

Finally, a TYPE=6 attrition is available which is essentially the same as TYPE=2 attrition except that the amount of material to be attrited is not specified as a fraction of the ash layer weight, but rather as the fraction of the total weight. Material needed to generate the specified attrition is first taken from the computed ash layer. If more material is needed, material is taken from the char enriched core.

BALANCE Module

The BALANCE module performs overall balances on the selected streams. Overall atom and energy balances are performed as well as kerogen-oil-coke balances useful in analyzing overall oil generation performance.

The kerogen-oil-coke balances look at changes in kerogen, oil, char and coke flow between input and output streams. Reaction stoichiometry from the kerogen pyrolysis reaction, reaction 12, and the oil coking reaction, reaction 16, are used to develop estimates of the relative amount of oil generation and coking occurring in the unit. These calculations assume that all three oils defined in the basic pyrolysis reaction (OIL-1, OIL-2 and OIL-3) coke with the same stoichiometry, on a weight basis, as Oil-1.

CNTR_CURRENT Module

The CNTR_CURRENT module is a reactor module tuned to allow a dilute solid phase counter-current flow reactor to be modeled. This module assumes that the process to be modeled is basically one in which solids and gases/liquids move in a counter-current fashion relative to each other. No spatial resolution is assumed and the well-mixed model is used to perform the required computations. The default assumption for transport correlations in this module is that single particle correlations using actual particle sizes are appropriate.

The well-mixed model requires effective densities of each component to be specified for reaction rate computations, as well as relative solid-gas velocities for use in transport correlations. Effective densities of solids in the reactor are determined by the user specified velocities for each solid stream, the HEIGHT of the unit, and input solid flow rates. The effective gas density in the reactor is computed from the averaged properties as defined by the gas weighting factor (for default outlet conditions are used). This module assumes the solid density in the reactor is small and it assumes the gas volume in the reactor is equal to the reactor volume. This means the module will not perform well for dense phase systems. Solid-gas velocities used in transport correlations are computed by adding the solid velocities, specified by the user, to the average gas velocity. The average gas velocity is computed using average gas properties and assuming the gas flow along the HEIGHT of the unit.

Since this reactor module was conceived to primarily look at dilute phase systems the well-mixed model radiative term can be invoked if desired to enhance gas to solid heat transfer.

CO_CURRENT Module

The CO_CURRENT module allows a dilute phase co-current plug-flow type reactor to be modeled. The PACKED_BED module should be used for dense phase systems. The gas and all solid streams may have separate velocities. This module uses the plug-flow model to perform calculations, consequently spatial changes are resolved in the course of the computations.

The plug-flow model uses velocities set by the user for each solid stream and it is assumed that these do not very as they move along the HEIGHT of the reactor. The

default assumption for transport correlations in this module is that single particle correlations using actual particle sizes are appropriate.

Since this reactor module was conceived to primarily look at dilute phase systems, the radiative term can be invoked if desired to enhance gas to solid heat transfer. In addition, transport of energy to/from the wall can be specified by defining the wall heat transfer coefficient to be nonzero and setting a wall temperature. When a nonzero wall heat transfer term is specified the module no longer is adiabatic.

CSTR Module

The CSTR module simulates a cstr reactor. The default parameters are tuned to represent a simple fluidized bed system with no bubble phase. No spatial resolution is assumed and the well-mixed model is used to perform the required computations. The default assumption for transport correlations in this module is that single particle correlations using a single average particle size are appropriate.

The well-mixed model requires effective densities of each component to be specified as well as relative solid-gas velocities for use in transport correlations. Effective densities of solids in the reactor are determined by the user specified void volume fraction in the reactor, BEDP. The distribution of solid streams within the reactor are determined, by default, from the ratio of input solid flow rates. Alternatively, the relative fractions of each input stream within the reactor can be specified. This distribution which influences particle concentrations of the solid streams within the reactor, and therefore the transport and reaction rates, are specified by input parameters. The effective gas density in the reactor is computed from the averaged properties as defined by the gas weighting factor (for default outlet conditions are used) and the bed porosity. A single solid-gas velocity is used in transport correlations for all particles. This velocity is the superficial gas velocity through the reactor assuming the direction of gas flow is along the reactor's HEIGHT. The properties and flow rate of the gas are taken from available estimates of the outlet gas properties.

ERROR Module

The ERROR module allows error criteria to be set on stream variables. This provides a means to insure convergence of stream properties in systems containing recycle streams on a basis other than temperatures. Stream flow rates, temperatures, and compositions can be used to set the error values.

Individual errors are calculated using the following formulas:

$$E = \frac{\left|F^N - F^O\right|}{F^N},$$

$$E = \frac{\left|T^N - T^O\right|}{T^N},$$

$$\text{and} \quad E = \frac{\left|\omega_i^N - \omega_i^O\right|}{\omega_i^N}.$$

Where F is flow rate, T is temperature and ω_i is mass or mole fraction of species i. The superscripts "N" and "O" refer to new and old values respectively. For cases in which very small mole or weight fractions are present the denominator is limited to be greater than or equal to $1x10^{-10}$.

In addition to the above errors, an additional error is also defined for solid stream particle diameters

$$E = \frac{\left|d_p^N - d_p^O\right|}{d_p^N}.$$

The final error is the sum of all the individual errors defined above. Each steam input/output pair is treated as a separate entity.

The old and new values are obtained from stream variables associated with the module. It is assumed that the input streams are the new values and the output streams prior to the module computations contain the old values. After completing the error computations the module sets the output stream values equal to the input stream values.

FLUID_BED Module

The FLUID_BED module allows a fluidized bed reactor to be modeled. The residence time in the reactor is determined by solids and gas flow rates, reactor size, and bed porosity.

Numerous references such as those by Yates (1983), Froment and Bischoff (1990), Kwauk and Kunii (1985), Howard (1983), Kunii and Levenspiel (1977), and Howard(1989), describe fluidized bed behavior. In most of these references, mathematical models that predict or describe the behavior are presented. In this section, we will neither review all of the references nor describe all of the models, but will instead, describe the two phase fluidized bed model that has been implemented into the OSP code.

A fluidized–bed is a reactor in which a dense material, normally a granulated solid is levitated or suspended by a less dense material, e.g. a gas, that is flowing up through the dense material. As the mixture of gas and solid churns, bubbles can form at the

bottom of the reactor and then move up through the churning mixture. Numerous measurements of the bubble phase indicate that the bubbles contain almost no solids. Therefore, virtually no solid-gas reactions occur in the bubble phase. Because the gas flowing in the bubbles doesn't react with the solid, the extent of reaction of the gas will be less than that predicted by a single phase will-mixed model. As the bubbles move up through the reactor, some gas is exchanged between the churning mixture of gas and solid that surrounds the bubbles, which is called the emulsion phase. The exchange rate between the emulsion and the bubble phases has been determined empirically, as a function of the bubble size, bubble velocity, and reactor diameter.

The two phase model of a fluidized bed used in OSP consists of a single region well-mixed sub model for the emulsion phase and a series of well-mixed sub models for the bubble phase. By using multiple well-mixed regions for the bubble phase, it is possible to simulate the motion of the bubbles rising up through the emulsion. As the bubbles rise, gas flows up from the lowest bubble region to the next lowest, continuing up to the top of the reactor. In addition, gas is exchanged between the bubble regions and the single well-mixed emulsion phase. The number of well-mixed sub models, or regions, used to simulate the bubble phase is a model parameter available which can be set by the user.

This approach is similar to that presented by Wen, et al.(1971). There are, however, several differences, for example, the size of the well-mixed regions describing the bubble phase are not controlled by the bubble size, a constant-average bubble size is used, and gas is assumed to flow out of the emulsion phase at the top of the reactor, rather than continuing to circulate in the emulsion.

As the bubbles rise through the emulsion and gas is exchanged between the bubbles and the emulsion, enthalpy and mass balances are maintained as the exchange occurs. As mentioned before, solid is only present in the emulsion and so the solid-gas reactions only occur there. However, since gas is exchanged between the emulsion and the bubble phase, gaseous products will enter the bubble phase.

At the top of the reactor, the gas from the emulsion and bubble phases is mixed. A molar weighted average is used to compute the final gas composition leaving the top of the fluidized bed reactor.

Equations Used in the Two Phase Model of a Fluidized Bed

The model used to simulate the two phase fluidized bed is as simple as possible, while including the important characteristics of the two phase phenomena. The equation used to predict the minimum fluidization velocity is that developed by Wen and Yu (1966). Chyang, et al. (1989) compared their experimental data and that of other researchers for minimum fluidization velocity for binary and polydispersed mixtures to empirical models reported by several researchers. Chyang and his coworkers found

that the equation developed by Wen and Yu fit the data better than any of the other models.

The other variables that must be determined, for the simplest two phase model of a fluidized bed, are the bubble velocity, bubble size, bubble volume fraction, and bubble-emulsion gas exchange rate.

Because this model is implemented into the larger code, OSP, the variables used in its simulation must be consistent with the variables passed to it from OSP. The molar flow rate of gas and the bed diameter were used to calculate the superficial gas velocity, U_S. An area weighted particle size was calculated from the particle sizes and mass flow rate of the solid streams.

The specific equations used in this model are listed below. The calculation begins with an estimate of the Reynolds number at minimum fluidization, Re_{mf}, as a function of the Archimedes number, Ar. The minimum fluidization velocity, U_{mf}, is then calculated from the Reynolds number. The other variables used in the correlation are the solid density, ρ_S, the particle size, d_p, the gravity constant, g, and gas viscosity, μ.

$$Ar = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2}$$

$$\mathrm{Re}_{mf} = (33.7^2 + 0.0408 Ar) - 33.7$$

$$U_{mf} = \frac{\mu \,\mathrm{Re}_{mf}}{d_p \rho_g}$$

Once the minimum fluidization velocity and the total superficial velocity, U_S, are known, the bubble size, D_b, bubble velocity, V_b, bubble volume fraction, f_b, and emulsion-bubble gas exchange rate, k_l, can be determined. Other variables used in the correlations are the bubble height, Z, the gravity constant, g, the crossectional area of the fluid bed, A_{fb}, the height of the fluid bed, L_{fb}, and the number of bubbles, n_b.

$$D_b = \alpha_b (1.0 + 27.2(U_S - U_{mf}))^{\frac{1}{3}} (1 + 6.82Z)^{1.21}$$

$$V_b = \beta_b \left(D_b g \right)^{0.5}$$

$$f_b = \frac{(U_s - U_{fm})}{V_b}$$

$$k_l = \frac{\lambda_b f_b U_{mf} A_{fb} L_{fb}}{D_b n_b}$$

The three coefficients, α_b, β_b, and λ_b are included in the above expressions to provide a convenient way to perform a simplified parameter sensitivity study of the two phase model. The nominal values of the coefficients were obtained from the same references as the equations themselves. The nominal values are 0.00853 m, 0.771 m/s, and 0.0714 respectively and were obtained from Davidson and Harrison (1971). These values are the default values used in the OSP code.

LIFT_PIPE module

The LIFT_PIPE module allows a dilute phase lift pipe to be modeled. The gas and all solid streams may have separate velocities. The solid velocities are obtained from input or computed slip velocities. This module uses the internal plug-flow model to perform the calculations. Part of the plug-flow assumption includes neglecting the radial variations of solid bulk density, solid velocity, and gas velocity. Computed slip velocities include the effect of solid-solid impact, and solid wall friction. The slip velocities are calculated using the gas and solid properties at the entrance of the lift-pipe. At the end of the calculation, the slip velocities of all solid streams are computed using the properties at both the entrance and exit of the lift, for comparison. The actual computations are performed, however, using only the slip velocities determined based on inlet gas and solid properties. Multiple LIFT_PIPE modules can be used to allow for variation of slip velocities up a lift-pipe in cases where these variations are significant.

Since this reactor module was conceived to primarily look at dilute phase systems, the radiative term can be invoked if desired to enhance gas to solid heat transfer. In addition, transport of energy to/from the wall can be specified by defining the wall heat transfer coefficient to be nonzero and setting a wall temperature. When a nonzero wall heat transfer term is specified the module no longer is adiabatic.

Details of the solid velocity calculations are given in the following two subsections.

Lift Pipe Particle Slip Velocities for a Distribution of Several Particle Size Classes

A method to include the affects of particles of differing size on the calculation of particle slip velocities was developed by Nakamura and Capes (1976). They reported both measurements of binary particle-particle interaction and a method of evaluating the interaction phenomena for dilute flow. (This work has been extended to a dense multiple size class mixture in a model of the hydrodynamics in a fluidized bed by Syamlal(1985).)

In the analysis of a lift pipe, the dilute flow approach presented by Nakamura and Capes (1976) is appropriate. The model suitable for a binary particle size distribution is extended to handle a multiple class size distribution of any number of size classes. The set of two equations previously used for the binary distributions had to be solved numerically, similarly the set of n equations described below in the multiple size class approach must also be solved numerically.

Derivation of the Multiple Particle Size Class Model

Using the approach presented by Nakamura and Capes (1976), a momentum balance on a section of the lift pipe is given below;

$$\frac{1}{g}\frac{\partial P}{\partial t} = (\rho_A x_A + \rho_B x_B)(1-\varepsilon) + \frac{4}{gD_t}(\tau_f + \tau_A + \tau_B)$$

Where, P, is the gas pressure, t is time, g is the gravity constant, ρ_A is the density of the size class with the smaller particle size, x_A is the mass fraction of the solid which has the smaller particle size, ρ_B is the density of the size class with the larger particle size, x_B is the mass fraction of the solid which has the larger particle size, ε is the void fraction, D_t is the lift pipe diameter, τ_f is the fluid-wall stress, τ_A is the solid A-wall stress, and τ_B is the solid B-wall stress.

A momentum balance on each size class can also be derived as;

$$x_A\beta_A\left[\frac{U_g}{\varepsilon} - \frac{U_A}{\varepsilon_A}(1-\varepsilon)\right]^2 - \frac{4\tau_A}{D_t} - \rho_A x_A g(1-\varepsilon) - I_{AB} = 0$$

$$x_B\beta_B\left[\frac{U_g}{\varepsilon} - \frac{U_B}{\varepsilon_A}(1-\varepsilon)\right]^2 - \frac{4\tau_B}{D_t} - \rho_B x_B g(1-\varepsilon) + I_{AB} = 0$$

Where U_g is the gas velocity and

$$\beta_A = \frac{\rho_A(1-\varepsilon)g}{V_{A,t}^2\varepsilon^{(2n-3)}}$$

$$\beta_B = \frac{\rho_B(1-\varepsilon)g}{V_{B,t}^2\varepsilon^{(2n-3)}}$$

$$\tau_A = \frac{C_A \rho_A U_A}{2}$$

$$\tau_B = \frac{C_B \rho_B U_B}{2}$$

The particle-particle interaction term, I_{AB}, has been defined by several researchers (for example, Samalal, 1985, Soo, 1976, and Muschelknautz, 1959). The term used by Nakamura and Capes is similar to that used by Soo and is given below:

$$I_{AB} = \gamma_{A,B} x_A x_B (1-\varepsilon)^2 \left[\frac{U_A}{x_A(1-\varepsilon)} - \frac{U_B}{x_B(1-\varepsilon)} \right]^2$$

$$\gamma_{A,B} = \frac{3\phi(1+\mathbf{e})\rho_A}{4\phi_s R_B} - \frac{\left[1+\frac{R_A}{R_B}\right]^2}{1+\frac{\rho_A}{\rho_B}\left(\frac{R_A}{R_B}\right)^3}$$

Where, ϕ is the particle-particle interaction factor which accounts for the effects of multiplicity of scattering and fluid viscous motion, the variable e is the restitution coefficient, ϕ_s is the sphericity and R_A and R_B are the particle radii of the two solids.

The derivation of the multiple solid size class analysis begins by extending the momentum equation to that for the i^{th} size class.

$$\varepsilon_i \beta_i \left[V_g - V_i \right]^2 - \frac{4\tau_i}{D_t} - \varepsilon_i \rho_i g + \sum_{k=1}^{j-1} I_{i,k} - \sum_{k=j+1}^{n} I_{i,k} = 0$$

Where, V_g is the gas velocity, V_i is the velocity of solid in size class i, τ_i is the solid-wall stress for size class i, D_t is the lift-pipe diameter, ε_i is the solid volume fraction for the size class i, g is the gravity constant, and I_{ik} is the particle-particle interaction term, which is defined as:

$$I_{i,j} = \gamma_{i,j} \varepsilon_i \varepsilon_j \left[V_i - V_j \right]^2$$

$$\gamma_{i,j} = \frac{3\phi(1+e)\rho_i}{4\phi_s R_j} \frac{\left(1+\frac{R_i}{R_j}\right)^2}{1+\frac{\rho_i}{\rho_j}\left(\frac{R_i}{R_j}\right)^3}$$

The equations are simplified substantially by using the volume fraction of the i^{th} solid size class, rather than the mass fraction of the solid feed stream, and the solid velocity of the i^{th} solid size class rather than the superficial velocities.

In this modeling approach, the terminal velocity of the particles in each size class is determined in the absence of particle-particle interactions. The single sphere terminal velocities have been calculated using the correlation developed by Haider and Levenspiel (1989) which is given below. Where, $V_{i,t}$ is the terminal velocity of particles in size class *i*, $\rho_{i,s}$ is the solid density of the solid in size class i, and $d_{i,\,sphere}$ is the spherical particle diameter of the particles in size class *i*.

Note that sphericity enters both the computation of the terminal velocity of an isolated particle and the interaction term for the assemblage.

$$V_{i,t} = V_{i,*}\left[\frac{\rho_g^2}{g\mu\left(\rho_{i,s}-\rho_g\right)}\right]^{-\frac{1}{3}}$$

$$V_{i,*} = \left[\frac{18}{d_{i,*}^2} + \frac{2.3348 - 1.7439\phi_s}{d_{i,*}^{0.5}}\right]^{-1}$$

$$d_{i,*} = d_{i,sphere}\left[\frac{g\rho_g\left(\rho_{i,s}-\rho_g\right)}{\mu^2}\right]^{\frac{1}{3}}$$

The set of n equations involving the n solid volume fractions and solid velocities is solved iteratively. Each of the momentum equations for each size classes is proportional to the rate of change of the velocity of the size class. Since desired solution of this set of equations occurs when all of the equations are equal to zero, and since the specific path to this state is not of immediate interest, the set of algebraic equations are recast as ordinary differential equations for the respective velocity for each equation. The gas velocity, void fraction, and the solid volume fractions are all recalculated

during each iteration. This set of ordinary equations is then solved using the ordinary differential equation solver LSODE.

MERGE_STRMS Module

The MERGE_STRMS module combines multiple input streams into a smaller number of output streams. All output streams are in thermal equilibrium (i.e. same temperature). The outlet temperature is determine by adiabatic mixing of all input streams in the absence of any reactions. Only one gas and one liquid stream can leave the module but multiple exiting solid streams can be defined by specifying mix-group membership.

PACKED_BED Module

The PACKED_BED module allows a dense phase co-current plug-flow type reactor to be modeled. The CO_CURRENT, or LIFT_PIPE modules should be used for dilute phase systems. This module uses the plug-flow model to perform the calculations, consequently spatial changes are resolved in the course of the computations.

The plug-flow model uses velocities established by the user set bed porosity, BEDP, and the inlet solid flow rate. All solids are assumed to move at a constant uniform velocity through the reactor. The default assumption for transport correlations in this module is that packed bed correlations using a single particle size are appropriate. Since this is a dense phase reactor no radiation transport is allowed.

PASS_THRU Module

The PASS_THRU module passes input streams straight through to output streams. This module is useful in making name changes and in isolating flow loops.

PHASE_CHANGE Module

The PHASE_CHANGE module allows phase changes between gases and liquids to be accomplished. Simple material balance algorithms are used, no phase equilibrium considerations are included. An explicit heat balance is done as part of the computations since it is assumed heat leaves / enters the system during the phase change and outlet temperatures as set by the user. Two types of phase change are handled: condensation, TYPE='C', and evaporation, TYPE='E'.

When executed in the condensation mode the module condenses selected components from an input gas stream and generates a separate liquid stream for each species condensed. Only those gas species having a corresponding liquid species may be condensed. There is a single temperature for the exiting gas and liquid streams. This

temperature is either specified by input, or the temperature of the input gas stream is used.

In the condensation mode this module can also be used to change the temperature of a gas stream. When used in this fashion an input and output gas stream are specified and the desired temperature set.

In the evaporation mode the module allows selected species in an input liquid stream to be evaporated into a gas stream. All liquid species can be evaporated. In this mode an input liquid stream and an output liquid and gas stream must be specified. An input gas stream is optional. There is a single temperature for the exiting gas and liquid streams. This temperature is either specified by input, or the temperature of the input gas stream is used.

PROP_TAB Module

PROP_TAB is a service module that prints out a table of all species properties over a range of temperatures.

RELAX Module

The RELAX module allows solid stream updating which blends old and new values of solid stream parameters. This relaxation to newly computed values is sometimes necessary to allow the steady-state condition of a recycle loop to be reached without unstable oscillations.

The new values are computed using

$$\Gamma^R = \xi_r \Gamma^N + (1 - \xi_r)\Gamma^O,$$

where ξ_r is the relaxation factor and the Γ can be solid flow rate, temperature, species composition, diameter or porosity. The superscripts "*R*", "*N*" and *"O"* referred to relaxed value, new value and old value respectively. The relaxed values are used to set the values of output streams.

The old and new values are obtained from stream variables associated with the module. It is assumed that the input streams are the new values and the output streams at the beginning of the module computations contain the old values.

SPLIT_STRMS Module

The SPLIT_STRMS module allows single streams to be split into two output streams. The splitting is done on a fractional absolute flow rate basis. This fractional split or absolute flow rate is applied to one of the outlet streams with the other carrying the remainder of the flow. It is also possible to use this module to multiply a stream flow by any real value. When used as a stream multiplier the second stream flow rate is set by the module to zero. Only one input gas and one liquid stream are allowed. Up to 10 solid input streams can be defined. For cases in which a set solid flow rate is desired the flow rate is applied to the sum of all the solid streams. The required solid is take in equal fraction from each input stream.

STOICH Module

The STOICH module determines the stoichiometry of a given reaction. Also, the heat of reaction over a selected temperature range can be computed. The user can optionally use the module to reset stoichiometric coefficients of a reaction. Unlike most other modules the computations done by this module are all done during the initialization phase. This module performs no calculations during the calculation phase of OSP's execution.

This module uses the stream information in a special way. Specification of stream composition and flow are used to set know stoichiometric coefficients of the reaction. As a consequence, negative mole fractions or weight fractions are meaningful and are use to designate reactants. The input composition multiplied by the streams flow rate are interpreted as the known stoichiometric coefficients. A single stream is used to specify all components of a given type. That is at most three streams are needed a solid, a gas and a liquid stream. The specification is completed by defining the reactants whose coefficients are to be computed and which atomic balances are to be employed. A "base" component is defined and the results are normalized so that this "base" component has a coefficient of one. It is the user's responsibility to pose a well defined problem. The module does some consistency checking and will report an error if it can determine the set of equations it needs to solve is under or over defined.

STOICH_REACT Module

The STOICH_REACT module allows a simple stoichiometric reactor to be modeled. The extent off reaction is specified by stoichiometric fractions based on input levels of reactants. The extent of reaction is based on the specified fraction of the limiting reactant.

One input gas and one liquid stream are considered, but multiple input solid streams can be utilized. If multiple solid streams are present then the

computation of limiting solid reactants use the sum of reactants in all solid streams. In apportioning the use of solid reactants the desired fraction is applied to each solid stream. That is the same fraction of the reactant present in each solid stream is consumed. If only solid products are present in a reaction and not solid reactants, then the fraction of product apportioned to each solid stream is made proportional to their flow rates.

Since stoichiometry is done relative to inlet amounts two step processes require the use of multiple modules (e.g. coking of gas phase oil). Also it is possible for the user input to require the consumption of more than the available amount of a reactant if it is consumed by more than one reaction. If this occurs an error message is given and calculations are terminated.

The outlet temperatures are computed based on adiabatic operation (with the possible addition or subtraction of a specified amount of heat), or by user specification of the outlet temperatures. In the later case the heat gain / loss is computed.

PARTICLE HEAT AND MASS TRANSFER COEFFICIENTS

Because the OSP code has been developed to study heterogeneous processes, gas-solid heat transfer calculations are an important consideration in the analysis. Several different environments can be analyzed using the OSP code, including dilute phase solids transport, the dense phase environment in a packed bed reactor, and a moderately dense phase environment in fluidized beds. Because of the variety of environments, two types of heat and mass transfer coefficients and two types of particle size averaging are available in the OSP code. One correlation is available for heat transfer between dilute flow particles and gas and a second is available for use in fluidized bed calculations . A parameter, IBED, is available to the user to switch between the single particle coefficient and the fluidized bed model. The similarity between heat and mass transfer coefficients is maintained, i.e.. if a single particle coefficient is used it is used for both heat and mass transfer.

The single particle heat and mass transfer correlations are given below:

$$Nu = 2 + 0.6\,\mathrm{Re}^{\frac{1}{2}}\,\mathrm{Pr}^{\frac{1}{3}}$$

$$Nu_m = 2 + 0.6\,\mathrm{Re}^{\frac{1}{2}}\,Sc^{\frac{1}{3}}$$

The fluidized–bed correlations are given below:

$$Nu = 2 + 1.8\,\mathrm{Re}^{\frac{1}{2}}\,\mathrm{Pr}^{\frac{1}{3}}$$

$$Nu_m = 2 + 1.8\,\mathrm{Re}^{\frac{1}{2}} Sc^{\frac{1}{3}}$$

where:

$$Nu = \frac{hd_p}{k}$$

$$Nu_m = \frac{h_m d_p}{cD_{im}}$$

$$\mathrm{Re} = \frac{V_r d_p \rho_g}{\mu}$$

$$\mathrm{Pr} = \frac{C_p \mu}{k}$$

$$Sc = \frac{\mu}{\rho_g D_{im}}$$

Where Re is the Reynolds number, Pr is the Prandtl number, Nu is the heat transfer Nusselt number, Nu_m is the mass transfer Nusselt number (or Sherwood Number), Sc is the Schmidt number, h is the particle-gas heat transfer coefficient, d_p is the particle diameter, k is the gas thermal conductivity, h_m is the particle-gas mass transfer coefficient, c is the total gas molar density, D_{im} is the appropriate binary diffusion coefficient, V_r is the gas-solid relative velocity, μ is the gas viscosity, and C_p is the gas heat capacity.

Another aspect of heterogeneous heat and mass transfer that is of concern is how to simulate effects that occur in mixtures of solids with a large range in particle size. Typically in the HRS process more than ten percent of the solid has a particle diameter of approximately 10μ. The rest of the solid has a diameter between 1 and 7 mm. The smaller particles will tend to effect the heat transfer coefficient between the gas and the larger particles. The small particles will reach thermal equilibrium with the gas very quickly. The small particles will tend to degrade the boundary layer around the larger particles, which will decrease the transport resistance into and out of the larger particles. This effect has been observed experimentally in fluidized bed pyrolysis/combustion experiments, in which large particles with a size of 3 to 7 mm are placed in a bed of sand particles that have a particle size of 0.2 mm. The effective heat transfer coefficient for the heat transfer from the bed of sand to the larger solid particle

could be best estimated using a coefficient based on the particle size of the sand, and not the particle size of the larger particle.

An approximate method of dealing with the influence of the small particles on the heat transfer to larger particles is to use an area weighted average particle size to calculate the heat transfer coefficient for all of the particulate solids. This approach will naturally approach both extremes. If little of the small particle solid is present, then a heat transfer coefficient based on the average size of the larger particles is reasonable. If a large amount of the smaller particles is present, then a large heat transfer coefficient will be calculated because of the decrease in resistance to heat transfer cause by the small particles. A parameter, IDILUTE, is set by the user in the input file to select which method should be used to calculate the particle size for the heat transfer coefficients.

PROCESS STREAM CHARACTERISTICS

In the OSP code, unit operation modules are connected with process streams. Three types of process streams are used, gas streams, solid streams and liquid streams. Each of the streams have stream variables associated with them. Each of the three stream types has flow rate, temperature and composition variables associated with them. The units for the flow rate of a gas stream is moles per second and the units for the flow rates of solid or liquid stream is kg per second. The temperature is maintained in Kelvin units and the composition of the gas streams are in mole fraction units while those for liquids and solids are weight fractions. Gas stream variables also include a pressure in Pascals.

The solid streams have several other defined stream variables. One group are auxiliary property variables. These variables are treated like compositions during combination and splitting processes . Three auxiliary properties are currently defined. The first is the original char content of the solid. This value is used by the attrition and char combustion models. The second is the original kerogen content of the solid. This property is used in estimating oxygen diffusivities in the char combustion model. The third value is used by the FeS_2 combustion models and it is the original density of FeS_2 in a particle. The particle size and porosity are also part of a solid stream characterization. If a distribution of solid size classes is used, then the distribution can be discretized into several separate streams each with appropriate particle size and flow rate.

REACTIONS

Currently OSP contains a set of 29 reactions which can be selected in each of the reactor modules. Rate expressions are available in OSP for the first 25 reactions. In the rate expressions, given below, for these reactions the rates are computed on the basis of the primary (base) reactant. Stoichiometric factors can then be used to obtain rates for other reactants and products. The rates are presented on a per-unit-volume of solid basis. In

practice these rates are multiplied by a particle volume in the reaction rate subroutine. The rates used by reactor models assumes a per-particle basis. In the rate expressions developed below ρ_X is the density of solid species "X" in a particle in kg per unit volume of particle, y_X is the mole fraction of gas species "X" in the gas phase, T is the solid temperature, $A_?$'s are frequency factors in $1/s$, $T_?$'s are Arrhenius activation temperatures in Kelvin, and r_k are reaction rates either in $kg/s/m^3$ for solids and liquids or $mol/s/m^3$ for gases.

Kerogen Combustion - Reactions 1-3

The first three defined reactions are used to describe combustion of three types of kerogen. These reactions are included to remove any small amounts of kerogen which may find there way into an oxidizing atmosphere. The kerogen is assumed to combust at a rate equal to its pyrolysis rate. OSP automatically sets the products of combustion to the appropriate quantities of CO_2, H_2O, SO_2, and NO_2 based on the composition of the kerogen. To insure burning only occurs when oxygen is present the actual rate is expressed as

$$r_k = y_{O2}\rho_{Ker}A_{Ker}\exp\left(\frac{-T_{Ker}}{T}\right),$$

There are three separate reactions (k=1 to 3) for each of the three kerogen species. The base reactant for the rate is kerogen.

Char Combustion - Reactions 4-8

The next five reactions are used to describe the burning of the five elemental char species used to simulate char in some cases. All are tied to a single kinetic formulation based on a shrinking core model. Selectable parameters include the initial char density for use in the geometry parameters of the shrinking core model, a frequency factor and an activation temperature for use in the basic kinetic rate, and a kerogen density and a multiplicative factor used in computing effective oxygen diffusivity into the combusting particles. The initial char density and the kerogen content are set indirectly by specifying a stream name from which the needed values are obtained. The intrinsic char combustion kinetics is assumed to be given by a rate expression which is first order in both oxygen and char

$$r_4^* = A_{ch}\exp\left(\frac{-T_{ch}}{T}\right)\rho_{Char-C}\,y_{O_2}\,RT_g$$

R is the ideal gas constant. The superscript "*" indicates that this is an intrinsic chemical kinetic rate and not the overall rate which will is developed below and includes transport resistances. An analogous expression for each of the char species is

written to define rates r_5^* through r_8^*. The same frequency factor and Arrhenius activation temperature are used in each case.

The shrinking core model is used to estimate the internal diffusional resistance and a gas film resistance is used to estimate external mass transfer effects. The overall rate of oxygen consumption by all the char combustion reactions is given by

$$r_{O2} = \left\{ \frac{1}{\sum_{k=4}^{8} \left(a_{Char-k} r_k^* \right)} + \frac{d_p \varphi_s R T_g}{6 h_m P y_{O2}} + \frac{d_p^2 \left[\left(\frac{\rho_{Char}^o}{\sum_{k=4}^{8} \rho_{Char-k}} \right)^{1/3} - 1 \right]}{12 D_e y_{O2} \frac{T_g}{T}} \right\}^{-1},$$

where a_{Char-k} is the appropriate stoichiometric coefficient to convert rates to an oxygen consumption basis, d_p is the particle diameter, φ_s is the particle sphericity, the index 4 through 8 refers to the five char components (C,H,N,S & O), ρ_{Char}^o is the sum of all char component densities in an uncombusted char particle, and D_e is the effective diffusivity of oxygen through the particle matrix. The char density in the uncombusted core is obtained from the first auxiliary property of the appropriate stream flow. The effective oxygen diffusivity is assumed to be a function of original kerogen content and temperature (Mallon and Braun, 1976) according to

$$D_e = D_{coef} T^{1.65} \rho_{Ker}^o,$$

where D_{coef} is a selectable coefficient and ρ_{Ker}^o is the original kerogen density of the raw shale.

The final char combustion rates in terms of the base reactants defined as the char components is obtained from the overall oxygen consumption and the relative char component densities and stoichiometric factors

$$r_k = r_{O2} \left[\frac{\rho_k}{\sum_{k=4}^{8} \left(a_{Char-k} \rho_{Char-k} \right)} \right].$$

The base reactants are the individual char components.

Carbonate Self Decomposition - Reactions 9 & 10

Three carbonate mineral reactions are defined in the current reaction set. Two which involve straight decomposition of carbonates are described in this section. A third reaction involving a reaction with SiO_2 is described in a later section.

One is a magnesium carbonate decomposition reaction meant to simulate the rate of decomposition of a mixed carbonate mineral such as dolomite.

$$MgCO_3 \Rightarrow MgO + CO_2.$$

The other a calcium carbonate (calcite) decomposition reaction

$$CaCO_3 \Rightarrow CaO + CO_2 .$$

An engineering rate expressions developed at LLNL (Lewis, 1986) was used to establish the form of the rates of the carbonate decomposition reactions. The magnesium carbonate decomposition rate is assumed given by

$$r_9 = k_{Dol}\ \rho_{Dol}$$

$$k_{Dol} = A_{Dol-1} \exp\left(\frac{-T_{Dol-1}}{T}\right)\left(1-\beta_{CO_2}\right) + A_{Dol-2} \exp\left(\frac{-T_{Dol-2}}{T}\right)\beta_{CO_2}$$

$$\beta_{CO_2} = \frac{y_{CO2}P}{1.013x10^5}$$

where k_{Dol} is constrained to be greater than or equal to zero. (i.e. the reverse reaction is not allowed) and has units of reciprocal seconds. The dependence on carbon dioxide partial pressure is based on experiments carried out with essentially no carbon dioxide present and with one atmosphere of carbon dioxide. The functional form simply allows reasonable interpolation between these two conditions. The carbon dioxide partial pressure is expressed in Pascal's. The rate is based on magnesium carbonate.

The calcium carbonate self decomposition is expressed in an analogous form.

$$r_{10} = k_{Cal,Self}\ \rho_{Cal}$$

$$k_{Cal,Self} = A_{Cal,Self} \exp\left(\frac{-T_{Cal,Self}}{T}\right)\left[1 - \frac{y_{CO2}P}{A_{CO2-EQ} \exp\left(\frac{-T_{CO2-EQ}}{T}\right)}\right]$$

As in the magnesium carbonate decomposition the rate constant is limited to values greater than or equal to zero. The rate is based on calcium carbonate.

Kerogen Pyrolysis - Reactions 11 & 12

Reactions 11 and 12 describe the pyrolysis of Kerogen-1. Reaction 11 assumes products will include oils in liquid form while reaction 12 is identical except default

stoichiometric factors assume that oils are produced as gases. The char produced in this reaction is assumed to the composite char species which has a fixed elemental ratio. If desired the individual char species can used if the stoichiometric coefficients for the reaction are properly redefined by the user input file.

The frequency factor and activation temperature are the same factors mentioned above which are used in the description of kerogen combustion. The basis for the reaction is kerogen.

$$r_k = \rho_{Ker} A_{Ker} \exp\left(\frac{-T_{Ker}}{T}\right),$$

where *k* is either 11 or 12.

Oil Adsorption Reactions - Reactions 13-15

The default stoichiometry for the kerogen pyrolysis reaction includes the production of three oils. These oils are associated with different boiling point fractions. Reactions are provided which allows adsorption of each of these three oils on internal solid surfaces to be modeled. Local equilibrium between internal gas phases and surfaces are assumed to be given by Langmuir type isotherms. The resistance for gas phase oil transport into and out of a particles is approximated using an external gas film resistance and an effective internal diffusion length which is represented by some fraction of the particle size. The primary parameters influencing the oil adsorption are the equilibrium coefficients for each oil and the effective internal area for oil adsorption. The Langmuir relation for the three oils is given by

$$K_i P_{O_i} = \frac{\theta_{O_i}}{1 - \sum_{i=1}^{i=3} \theta_{O_i}}$$

where θ_{O_i} is the fractional coverage of sites by Oil-*i*, K_i is an adsorption coefficient for Oil-*i*,, and P_{O_i} is the partial pressure of Oil-*i*, in the gas. θ_i is related to the surface concentration of oil by

$$\theta_{O_i} = \frac{\rho_{O_i}}{A_s M_{O_i} N^o S}$$

where ρ_{O_i} is the concentration of Oil-*i*, adsorbed on the particle on a mass per unit volume basis, A_S is the particle internal surface area per unit volume, M_{O_i} is the molecular weight of Oil-*i*,, N^o is Avagardo's number, and *S* is the number of sites per unit internal area. The equilibrium constant K_i is assumed to be a function of temperature according to

$$K_i = A_{K_i} \exp\left(\frac{T_{K_i}}{T}\right).$$

The adsorption rates are determined by the equilibrium relations, external and internal mass transfer resistances.

$$r_k = \left[\frac{6}{d_p \varphi_s}\right]\left[\frac{1}{\frac{1}{h_m} + \frac{d_p \delta_{Coke}}{D_e^{Oi}}}\right]\left[C_{O_i} - \left(\frac{\theta_{O_i}}{RTA_{K_i}\exp\left(\frac{T_{K_i}}{T}\right)}\right)\left(\frac{1}{1-\sum_{i=1}^{3}\theta_i}\right)\right],$$

where D_e^{Oi} is the effective diffusivity of oil *i* in the particle matrix, δ_{Coke} is a diffusion length expressed as a fraction of the particle size, and C_{O_i} is the concentration (mol/m^3) of oil vapor *i* in the gas phase. The diffusion length was determined from more detailed modeling work (Cena, 1991) as approximating the internal mass transfer resistance for oil diffusion during coke deposition on the interior of particles.

The effective diffusivities are defined in terms of oil/mixture diffusivities using the factor ε_s^2 to account for both the reduced cross section for diffusion and the tortuosity of the internal porosity. The oil/mixture diffusivities are obtained from the Fuller, Schettler & Giddings correlation (Reid, Prausnitz and Sherwood, 1977)

$$D_e^{O_i} = \varepsilon_s^2 \left\{ \frac{10^{-7} T^{1.75} \sqrt{\frac{M_{O_i} + M_m}{1000 M_{O_i} M_m}}}{P_{1.01x10^5}\left[\left(\sum v\right)_{O_i}^{1/3} + \left(\sum v\right)_m^{1/3}\right]^2} \right\}$$

where $\left(\sum v\right)_{O_i}$ is the sum of the atomic diffusion volumes for Oil-*i*. The *"m"* subscripts refer to a mixture value which are generally taken as values for the dominant gas species (e.g. nitrogen). The atomic diffusion volumes for simple gas species are given by tables. Those for the oils are obtained from incremental atomic diffusion volumes assuming the oils are made of CH_2 units and the number of the these units can be determined from the assumed oil molecular weights using $n = M_i/0.014$, where *n* is the number of units.

Oil Coking Reactions - Reactions 16-18

Each of three oils once adsorbed can undergo coking according to a first order rate expression with the rate constant given by

$$k_{O_i} = A_{O_i} \exp\left(\frac{-T_{O_i}}{T}\right)$$

The rate is assumed to be effective on mineral surfaces within the particle. Once these surfaces are covered by a layer of coke the rate is assumed be only a fraction, γ of the basic coking rate. This fraction of total surface area covered with coke, *a*, is assumed to be a function of average coke content of a particle according to the relation

$$\eta = \frac{\rho_{Coke} b_c}{A_s}$$

where b_C is the area covered per unit weight of coke.

The basis for the coking reactions is adsorbed oil and the rates are

$$r_k = \rho_{O_i} k_{O_i} \left[(1-\eta) + \eta\gamma \right]$$

where k is 16-18 for Oil 1-3 respectively and ρ_{O_i} is the density of adsorbed Oil-i in kg/m^3 of particle.

Coke Combustion - Reaction 19

Coke combustion is handled in an approximate fashion. An intrinsic rate expression is used but the internal diffusional resistance is handled by a characteristic length (much like in the oil adsorption). A gas film resistance is used to handle external transport. The combustion rate in terms of oxygen consumption is

$$r^*_{Coke_{O2}} = \left[\frac{\varphi_s d_p}{6h_m} + \frac{\varphi_s d_p \delta_{Coke_{O2}}}{6D_e} + \frac{1}{\left| a_{Coke_{O2}} \right| A_{Coke_{O2}} RT_g \rho_{Coke} \exp\left(\frac{-T_{Coke_{O2}}}{T} \right)} \right]^{-1},$$

where $\delta_{Coke_{O2}}$ is a diffusion length expressed as a fraction of the particle size. The basis for the reaction is coke and the final rate is

$$r_{19} = \frac{r^*_{Coke_{O2}}}{a_{Coke_{O2}}}.$$

Currently the coke combustion rates are calculated independent of other combustion reactions (e.g. char or FeS_2). In terms of transport of oxygen all the combustion reactions should be considered together. The problem is that unlike the char and the FeS_2 the location of coke within a particle is not easily characterized by its concentration level. For the most part the coke is deposited on the outer portion of the particle and at levels much lower than the char. Consequently, for simplicity its combustion is currently considered without regard to the char combustion. The treatment of combustion is a likely candidate for future model improvement.

Oil Evaporation - Reactions 20-22

Reactions 20-22 allow for the vaporization of Oils 1-3. These rates are not based on a physical model. They are included only to allow heat effects for oil vaporization to be correctly integrated into a reactor module. The assumption is that the oils will evaporate rapidly and essentially to completion. A set of three scale factors can be input to modify the rate of vaporization. Values should be used that provide for rapid

enough evaporation to vaporize all the liquid oil but not so fast as to cause undue difficulties in the computations of a given reactor module. The rates are based on evaporation of liquid oil and are given by

$$r_k = F_{O_i}\left(\frac{d_p}{0.002}\right)^3 \rho_{O_i}^l,$$

where F_{O_i} is a constant, and the reaction numbers, *k*, run from 20-22 for Oil-1 to Oil-3. Since all rates defined to date have involved heterogeneous solid / gas reactions, these evaporation rates are computed for each solid stream. The second factor which includes the particle diameter is included to help scale the rate as a function of particle size. The liquid oil concentration, $\rho_{O_i}^l$, is a relative concentration related to solid flows using

$$\rho_{O_i}^l = \frac{x_{O_i}^l F_l}{F_s},$$

where $x_{O_i}^l$ is the weight fraction of Oil-*i*, F_l is the liquid flow rate, and F_s is the total solid flow rate. These rates are formulated in this fashion to allow straightforward implementation into the current rate scheme and not because of any correspondence to underlying physics.

Composite Char and FeS_2 Combustion - Reactions 23 and 24

The kinetics for the combustion of the composite char species (reaction 23) is implemented using a shrinking core model. The equations used are similar to those already described for the combustion of elemental char species, except the summations are not required. In the absence of FeS_2 combustion the kinetic model is functionally identical to the elemental char combustion model and uses the same reaction parameters. The basis for the reaction rate is the char.

The combustion kinetics for FeS_2 is implemented in an approximate way using a shrinking core model. The net combustion reaction stoichiometry is given by the following

$$FeS_2 + 2CaCO_3 + 3.75O_2 \rightarrow 0.5Fe_2O_3 + 2CaSO_4 + 2CO_2.$$

The model assumes that the shrinking core is defined by the removal of FeS_2. The chemical kinetic expression makes the simple assumption that the rate is first order in FeS_2 and oxygen, with no implicit dependence on $CaCO_3$. That is, it assumes the carbonate is present in excess. In the absence of composite char combustion, the equations used are identical to those already described for the combustion of elemental char species. The only difference is that only a single solid species is considered (the FeS_2), therefore the summation over solid species is not required. A pre-exponential factor and an activation temperature are defined to allow them to be set independently of those for char composition. The original FeS_2 concentration is obtained from the third auxiliary solid property. The basis for the reaction rate is the FeS_2.

There is some interaction between the composite char combustion reaction and the FeS_2 combustion present in the current kinetic model when they are both active. This is

done, as described below, by using a composite oxygen flux when considering the diffusive contribution to the limitation of reaction rates.

It is not possible to define a simple geometric picture for a system in which there are potentially two shrinking cores present. Thus, even a semi-rigorous model based on the shrinking core concept is not possible when two reactions are considered. In practice most the combustion in systems of interest take place in diffusion control or chemical kinetic control, not in a mixed resistance system. In both the composite char and FeS_2 combustion reactions simple first order engineering chemical kinetic rates are used. In a shrinking core formulation, when the chemical kinetics is the limiting rate, the rates of combustion for two combustion reactions will be properly computed, within the limitations of the simplified chemical kinetic expressions. In the diffusion controlled regime, on the other hand, there is an interaction in overall computed rates because oxygen for both reactions must diffuse through the gas boundary layer and into the particle. To capture some of this interaction the net oxygen flux in the shrinking core models for composite char and FeS_2 combustion is taken to be the sum of the fluxes feeding both reactions. The size of the core needed by the model is set based on the remaining solid reactant for the reaction which has the fastest chemical rate under the prevailing conditions. In this way high rates by either reaction will in general reduce the rate of the other reaction in a manner, at least qualitatively, similar to the true physical process.

Calcite SiO_2 - Reaction 25

To complete the engineering rate expressions for calcite (calcium carbonate) decomposition a reaction involving SiO_2 is defined. The reaction stoichiometry is

$$CaCO_3 \quad + \quad SiO_2 \Rightarrow CaSiO_3 \quad + \quad CO_2 .$$

The calcite decomposition consists of a self decomposition reaction which is highly inhibited by the presence of carbon dioxide and the calcite / quartz reaction having a form similar to that of the dolomite decomposition.

$$r_{25} = k_{Cal,Quartz}\ \rho_{Cal}$$

$$k_{Cal,Quartz} = A_{Cal,Quartz-1} \exp\left(\frac{-T_{Cal,Quartz-1}}{T} \right)\left(1 - \beta_{CO_2}\right) + A_{Cal,Quartz-2} \exp\left(\frac{-T_{Cal,Quartz-2}}{T} \right)\beta_{CO_2}$$

The β_{CO2} is the same factor as defined in the $MgCO_3$ decomposition reaction and depends on carbon dioxide levels in the gas phase. As in the $MgCO_3$ decomposition described above, the dependence on carbon dioxide partial pressure is based on experiments carried out with essentially no carbon dioxide present and with one atmosphere of carbon dioxide. The functional form simply allows reasonable interpolation between these two conditions. No concentration of SiO_2 appears explicitly in the reaction kinetics, it is therefore assumed that the SiO_2 is always present in excess. The rate is based on calcium carbonate.

Default Reaction Parameters

All the reaction parameters introduced above have been given default values in OSP. Tables 1-7 present these default values, list the names used by OSP for input, and indicate the reference from which the default values where obtained.

Table 1. Default Parameters for Char Combustion - Reactions 4-8 and 23.

Parameter	OSP Name	Value	Units	Reference
A_{Ch}	A_CHAR_COMB	1.97×10^{6}	1/s	Fujimoto *et al.*,, 1986
T_{Ch}	T_CHAR_COMB	20202	^{o}K	*ibid.*
D_{coef}	DEO2_COEF	1.04×10^{-15}	$m^{5}/(s\ kg\ ^{o}K^{1.65})$	Mallon & Braun, 1976

Table 2. Default Parameters for Carbonate Decomposition Reactions 9, 10 and 25.

Parameter	OSP Name	Value	Units	Reference
A_{Dol-1}	A_DOL(1)	4.08×10^{7}	1/s	Lewis, 1986
T_{Dol-1}	T_DOL(1)	23320	^{o}K	*ibid.*
A_{Dol-2}	A_DOL(2)	9.02×10^{4}	1/s	*ibid.*
T_{Dol-2}	T_DOL(2)	17010	^{o}K	*ibid.*
$A_{Cal,Self}$	A_CAL(1)	1.3×10^{10}	1/s	*ibid.*
$T_{Cal,Self}$	T_CAL(1)	27680	^{o}K	*ibid.*
$A_{Cal,Quartz-1}$	A_CAL(2)	5.6×10^{8}	1/s	*ibid.*
$T_{Cal,Quartz-1}$	T_CAL(2)	29620	^{o}K	*ibid.*
$A_{Cal,Quartz-2}$	A_CAL(3)	8.53×10^{12}	1/s	*ibid.*
$T_{Cal,Quartz-2}$	T_CAL(3)	40460	^{o}K	*ibid.*
A_{CO2-EQ}	A_PCO2	1.94×10^{13}	Pa	*ibid.*
T_{CO2-EQ}	T_PCO2	22360	^{o}K	*ibid.*

Table 3. Default Parameters for Kerogen Pyrolysis - Reactions 11 & 12

Parameter	OSP Name	Value	Units	Reference
A_{Ker}	A_KER	2.81×10^{13}	$1/s$	Campbell & Koskinas, 1976
T_{Ker}	T_KER	26390	^oK	*ibid.*

Table 4. Default Parameters for Oil Adsorption & Coking - Reactions 13 & 18

Parameter	OSP Name	Value	Units	Reference
M_{O_1}	-	0.1549	kg/mol	Wallman *et al.*, 1991
M_{O_2}	-	0.338	kg/mol	*ibid.*
M_{O_3}	-	0.4507	kg/mol	*ibid.*
A_{O_i} (i=1 to 3)	A_COKE(1)	1.01×10^{10}	$1/s$	*ibid.*
T_{O_i} (i=1 to 3)	T_COKE(1)	19270	^oK	*ibid.*
A_{K_i} (i=1 to 3)	A_ADS(I)	3.0×10^{-7}	$1/Pa$	*ibid.*
T_{K_1}	T_ADS(1)	4730	^oK	*ibid.*
T_{K_2}	T_ADS(1)	6730	^oK	*ibid.*
T_{K_3}	T_ADS(1)	7730	^oK	*ibid.*
A_s	SOLID_INT	1×10^7	$1/m$	*ibid.*
S	NS_ADS	1.2×10^{18}	$sites/m^2$	*ibid.*
δ_{Coke}	DEL_COKE	0.105	-	*ibid.*
b_c	A_COKE	1.7×10^6	m^2/kg	*ibid.*
γ	COKE_FAC	0.1	-	*ibid.*

Table 5. Default Parameters for Coke Combustion - Reaction 19

Parameter	OSP Name	Value	Units	Reference
$A_{Coke_{O2}}$	A_COKE_COMB	1.97×10^6	$1/s$	none
$T_{Coke_{O2}}$	T_COKE_COMB	20202	^oK	none
$\delta_{Coke_{O2}}$	DEL_COKE_COMB	0.105	-	none

Table 6. Default Parameters for Oil Evaporation - Reactions 20-22

Parameter	OSP Name	Value	Units	Reference
F_{O_i} (i=1 to 3)	A_EVAP	1	kg/particle/s	none

Table 7. Default Parameters for FeS_2 Combustion - Reaction 24

Parameter	OSP Name	Value	Units	Reference
A_{Ch}	A_FES2_COMB	1.97×10^{6}	1/s	none
T_{Ch}	T_FES2_COMB	20202	^{o}K	none
D_{coef}	DEO2_COEF	1.04×10^{-15}	$m^5/(s\ kg\ ^{o}K^{1.65})$	Mallon & Braun, 1976

GENERAL COMPUTATIONAL SCHEME

Computations within each module are performed independent of other modules. Each module invokes a specific scheme tailored to its needs. In a given run a group of modules is selected to simulate a desired process. In some cases no recycle streams are present and one pass through each module will yield the desired result. On the other hand, it is very common for at least one recycle stream to be present. In this case iteration is required to reach the desired solution.

OSP iterates to a solution using simple functional iteration. The functional iteration is implicit in the structure of OSP since as stream results are computed by any module they are placed in the stream data base and are then used by all modules performing subsequent calculations. OSP continues computations, that is looping through all computational modules until an error criteria for the overall solution is met. The overall criteria is simply the maximum of the error from any individual module. Most modules have a defined error criteria based on the relative change between newly computed stream results and previously computed results. For all modules, except the ERROR module, these are based on normalized temperature changes. These error estimates are passed to the controller portion of OSP by each module. The user determines the overall error criteria by setting the TOL variable in the $GENERAL input.

If the temperature is not deemed a sufficient criteria for convergence, or if for other reasons error results from a module will not lead to the desired measure of convergence, the ERROR module can be used. It allows criteria to be set on other aspects of the stream variables. The errors are defined based on the difference between stream values on the current and the immediately preceding computational loop.

OSP also provides a means of iterating on loops internal to the overall computational loop involving all defined modules. This is done be defining computational groups. A computational group should represent an internal recycle loop. It must be composed of modules which are contiguous in the overall computation scheme. Multiple computational groups are supported. Each group can have any number of members, but the groups must not overlap. Group membership for a module is defined by setting the GROUP variable in the module input section. Each computation group is executed a specified number of times on each overall loop iteration. The number of times to execute a group is set by the GROUP_LOOP parameter in the $GENERAL input block.

Criteria which determine the accuracy of the calculations for a given module are in general not available for alteration by the user. Criteria have been selected that insure sufficient precision of the solutions. Certain of the reaction modules are exceptions. The reaction modules, except for the STOICH_REACT module, all rely on routines which implement the plug-flow or well-mixed model. These routines in turn use the LSODE software to perform the required numerical solutions. For the modules using the well-mixed model an error tolerance used by LSODE can be set by the user. This has been provided to allow solution of difficult systems to be accomplished, but also allows the use of looser tolerances for easier problems.

NOMENCLATURE

a_{Char-k} = Stoichiometric Coefficient for Combustion Reaction involving the k^{th} Char Species.

a_{ij} = Stoichiometric Coefficient for Reaction *j* and Solid Species *i*

A = Reactor Cross Sectional Area, m^2.

$A_{Cal,Self}$ = Frequency Factor Used in $CaCO_3$ Decomposition Reaction, $1/s$.

$A_{Cal,Quartz-1}$ = Frequency Factor Used in $CaCO_3$ Decomposition Reaction, $1/s$.

$A_{Cal,Quartz-2}$ = Frequency Factor Used in $CaCO_3$ Decomposition Reaction, $1/s$.

A_{Ch} = Frequency Factor for the Char Combustion Reaction, $1/s$.

A_{CO2-EQ} = Equilibrium Coefficient Used in $CaCO_3$ Decomposition Reaction, Pa.

$A_{Coke_{O2}}$ = Frequency Factor for the Coke Combustion Reaction, $1/s$.

A_{Dol-1} = Frequency Factor Used in $MgCO_3$ Decomposition Reaction, $1/s$.

A_{Dol-2} = Frequency Factor Used in $MgCO_3$ Decomposition Reaction, $1/s$.

A_{fb} = Cross Sectional Area of Fluidized Bed Reactor, m^2.

A_{Ch} = Frequency Factor for the FeS_2 Combustion Reaction, $1/s$.

A_{Ker} = Frequency Factor for the Kerogen Pyrolysis Reaction, $1/s$.

A_{K_i} = Coefficient for Adsorbed Oil-*i* Equilibrium Constant, $1/Pa$.

A_{O_i} = Frequency Factor for the Oil-*i* Coking Reaction, $1/s$.

A_p = Particle External Area, m^2.

Ar = Archimedes Number.

A_s = Particle Internal Surface Area per Unit Volume of Particle, $1/m$.

b_c = Area covered per Unit Weight Coke Deposited, m^2/kg.

c = Total Molar Concentration, Moles / m^3.

c_g = Effective Gas Heat Capacity, J / (mol K).

c_l = Effective Liquid Heat Capacity, J / (kg K).

c_s = Effective Solid Heat Capacity, J / (kg K).

C_i = Wall Viscous Stress Coefficient, m / s.

d^* = Dimensionless Particle Size Used in Haider, Levenspiel Correlation.

d_p = Particle Diameter, m.

D_{fb} = Bubble Diameter, m.

D_t = Lift Pipe Diameter, m.

D_{coef} = Coefficient Used in Determining D_e, m^5 / (kg s $^oK^{1.65}$)

D_e = Effective Diffusivity of Oxygen through Particle Matrix, m^2 / s.

D_e^{Oi} = Effective Diffusivity of Oil-*i* through Particle Matrix, m^2 / s.

D_{im} = Diffusivity of Gas Species *i* in Mixture, m^2 / s.

e = Coefficient of Restitution of Solid.

f_b = Bubble Volume Fraction in Fluidized Bed.

F_g = Flow Rate of Gas, mol / s.

F_{g_i} = Flow of Gas Species *i*, mol / s.

F_l = Flow Rate of Liquid, kg / s.

F_{l_i} = Flow of Liquid Species *i*, kg / s.

F_s = Flow Rate of Solid, kg / s.

F_{s_i} = Flow of Solid Species *i*, kg/s.

F_{O_i} = Constant in Oil-*i* Evaporation Reaction Rate, 1/s.

g = Gravity Constant, m^2/s.

h = Particle-Gas Heat Transfer Coefficient, $J/(m^2 \text{ sec } K)$

h_m = Particle-Gas Mass Transfer Coefficient, $mol/(m^2 \text{ sec})$

H_{g_i} = Enthalpy of Gas Species *i*, J/mol.

H_{l_i} = Enthalpy of Liquid Species *i*, J/kg.

H_R = Heat of Reaction, J/s/particle.

H_{s_i} = Enthalpy of Solid Species *i*, J/kg.

$I_{i,i}$ = Particle-Particle Drag Term.

k = Gas Thermal Conductivity, J/(m s K)

k_l = Bubble-Emulsion Gas Exchange Rate, m^3/s.

K_i = Equilibrium Constant for Oil-*i* adsorption, 1/Pa.

L_{fb} = Fluidized Bed Height, m.

M_{O_i} = Molecular Weight of Oil-*i*, kg/mol.

n_b = Number of Bubble Regions Used in Two Phase Fluid Bed Model.

n_g = The Number of Gas Species.

n_l = The Number of Liquid Species.

n_p = Number of Particle Streams.

n_s = The Number of Solid Species.

N^o = Avagadro's Number, 6.02×10^{23} molecules/mol.

N_p = Number of Particles per Unit Volume, $\#/m^3$.

Nu = Nusselt Number for Heat Transfer.

Nu_m = Nusselt Number for Mass Transfer (Sherwood Number)

P = Pressure, Pa.

P_{O_i} = Partial Pressure of Oil-*i*, Pa.

q_{rad} = Radiation Transport Term, $J/s/m^2$.

r_j = Rate of Reaction *j* per Unit Volume, $kg/s/m^3$.

R = Gas Constant, 8.314 $J/mol/^oK$

R_j = Rate of Reaction *j* per Particle, $kg/s/particle$

Re = Reynolds Number.

Re_{mf} = Reynolds Number at Minimum Fluidization.

R_t = Radius of Lift Pipe, m.

S = Active Coking Sites per Unit Area, $1/m^2$.

Sc = Schmidt Number.

S_{g_i} = Reaction Source(+)/Sink(-) of Gas Species *i*, $mol/s/m^3$.

S_{l_i} = Reaction Source(+)/Sink(-) of Liquid Species *i*, $kg/s/m^3$.

S_{s_i} = Reaction Source(+)/Sink(-) of Solid Species *i*, $kg/s/m^3$.

t = Time, s.

T = Temperature, ^oK.

$T_{Cal,Quartz-1}$ = Activation Temperature Used in $CaCO_3$ Decomposition Reaction , ^oK.

$T_{Cal,Quartz-2}$ = Activation Temperature Used in $CaCO_3$ Decomposition Reaction , ^oK.

$T_{Cal,Self}$ = Activation Temperature Used in $CaCO_3$ Decomposition Reaction , ^{o}K.

T_{Ch} = Activation Temperature for Char Combustion Reaction , ^{o}K.

$T_{Coke_{O2}}$ = Activation Temperature for Coke Combustion Reaction , ^{o}K.

T_{CO2-EQ} = Activation Temperature Used in $CaCO_3$ Decomposition Reaction, ^{o}K.

T_{Dol-1} = Activation Temperature Used in $MgCO_3$ Decomposition Reaction , ^{o}K.

T_{Dol-2} = Activation Temperature Used in $MgCO_3$ Decomposition Reaction , ^{o}K.

T_{Ch} = Activation Temperature for FeS_2 Combustion Reaction , ^{o}K.

T_g = Gas Phase Temperature, ^{o}K.

T_{Ker} = Activation Temperature for Kerogen Pyrolysis Reaction , ^{o}K.

T_{K_i} = Temperature Parameter Used in Defining Adsorbed Oil-*i* Equilibrium, ^{o}K.

T_{O_i} = Activation Temperature for Oil-*i* Coking Reaction , ^{o}K.

T_s = Solid Phase Temperature, ^{o}K.

T_w = Wall Temperature, ^{o}K.

U_{mf} = Minimum Fluidization Superficial Velocity, m / s.

U_s = Gas Superficial Velocity in Fluidized Bed, m / s.

v_s = Particle Velocity, m / s.

v_f = Radiation View Factor.

V_i = Velocity of Solid in Size Class i, m / s.

$V_{i,t}$ = Terminal Velocity of Solid in Size Class i, m / s.

V = Reactor Volume, m^3.

V_b = Bubble Velocity, m / s.

$V_{i,*}$ = Dimensionless Velocity Used in Haider, Levenspiel Correlation.

V_p = Particle Volume, m^3.

V_r = Relative Velocity Between Gas and Solid, m / s.

x_i = Mass Fraction of Solid with Particle Size d_i.

$x_{O_i}^l$ = Weight Fraction Oil-*i*.

x_{s_i} = Mass Fraction of Solid Species *i*.

y_{CO2} = Mole Fraction Carbon Dioxide.

y_{O2} = Mole Fraction Oxygen.

z = Dimension in Flow Direction, m.

Z = Fluidized Bed Height, m.

Greek Symbols

α_b = Bubble Diameter Coefficient, m.

β_b = Bubble Velocity Coefficient.

β_{CO2} = Carbon Dioxide Rate Factor for $MgCO_3$ $CaCO_3$ Decomposition Reactions.

β_l = Fluid Particle Drag Coefficient.

γ = Rate Reduction Factor for Coking Reactions.

δ_{Coke} = Fractional Diffusion Length Parameter for Oil Diffusion into Particles.

$\delta_{Coke_{O2}}$ = Fractional Diffusion Length Parameter for Oxygen Diffusion into Particles in Coke Combustion Reaction.

ε = Void Fraction in Lift Pipe.

ε_{ι} = Solid Volume Fraction of Size Class i in Lift Pipe.

ε_r = Emissivity.

ε_s = Internal Particle Porosity.

η = Fraction of Surface Covered by Coke.

θ_{O_i} = Fractional Coverage of Oil-*i* Used in Oil Adsorption Relations.

λ_b = Bubble-Emulsion Gas Exchange Rate Coefficient.

μ = Gas Viscosity, $kg/(m\ s)$

ξ_r = Relaxation Parameter.

ρ^{o}_{Char} = Sum of all Char Species Densities in an Uncombusted Particle, kg/m^3.

ρ_{Char-k} = Density of the k^{th} Char Component, kg/m^3.

ρ_g = Gas Density, kg/m^3

ρ^{o}_{Ker} = Kerogen Density in Raw Shale Used in Determining D_e , kg/m^3.

ρ^{*}_{i} = Intrinsic Density of Solid Species *i*, kg/m^3

ρ_{O_i} = Density of Adsorbed Oil-*i*, in a Particle kg/m^3.

$\rho^{l}_{O_i}$ = Relative Liquid Oil-*i* Used in the Oil Evaporation Reaction Rate.

ρ_s = Solid Density, kg/m^3

ρ^{*}_{s} = Density of the Solid Matrix Material, kg/m^3

σ = Steffan-Boltzmann Constant, $5.67x10^{-8}\ J/{}^{o}K^4/m^2$.

τ_{ι} = Wall-Solid Size Class i Viscous Stress Term, $kg\ m^2/s^2$.

φ_s = Particle Sphericity.

Subscripts

A = Refers to Size Class with Smaller Diameter in the Binary Particle-Particle Lift Pipe Model.

B = Refers to Size Class with Larger Diameter in the Binary Particle-Particle Lift Pipe Model.

g = Refers to Gas.

s = Refers to Solid.

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